

**RECOMMENDATIONS OF THE EXPERT PANEL ON  
THE EPA SPECIATION NETWORK  
FINAL SUMMARY-8/3/99  
By Petros Koutrakis, Chair  
Speciation Expert Panel**

**SUMMARY**

The expert panel met on May 18-19, 1999, in Las Vegas, NV, to review the EPA's revised guidance document on the speciation network. Members of the panel are: Drs. Tom Cahill, Phil Hopke, Lara Gundel, John Ondov, and Petros Koutrakis. Members of the speciation group, which consists of EPA staff and representatives from several states, also participated in this meeting. Below is a summary of the expert panel recommendations. Overall, the panel was impressed with the progress made since the last review held in Seattle a year ago. Most of the panel and working group recommendations were considered and have been incorporated into the Guidance Document. The panel strongly believes that the goals, objectives, and monitoring strategy of the Speciation Network are sound and have been communicated to a great extent to the states and the scientific community. The revised Guidance Document will help to inform the stakeholders further about the different aspects of this program.

1. Organize the Guidance Document in editions with web links. The link site-appended documents should be updated to reflect any changes that occur; thus, the Guidance Document will remain a living document.
2. Form a steering committee to oversee the speciation network. This committee should include scientists from OAQPS, ORD, and the states. Also, a team of permanent EPA staff should be assigned to coordinate the speciation network as soon as possible.
3. Adopt performance standards for the speciation samplers. Having the flexibility to employ more than one sampling technique will encourage researchers and manufactures to continue the development of integrated and continuous technologies. The development of continuous measurement techniques for sulfate, carbon, nitrate, and elements will be critical in reducing both labor and analysis costs. This report presents a series of performance criteria based on which the speciation samplers can be tested.
4. Conduct comprehensive sampling and analysis methods evaluations. Performance evaluation of organic measurement methods should be of high priority. These efforts should be continuous and span through the entire life of the network. Based on the findings of these studies, the network should be upgraded as needed. To balance network continuity and new technology, a set of guidelines should be developed in the near future. Based on these criteria, decisions should be made whether new sampling or analysis methods could be incorporated to the network.

## INTRODUCTION

The expert panel met on May 18-19 in Las Vegas, NV, to review the EPA's revised guidance document on the speciation network. Members of the panel are: Drs. Tom Cahill, Phil Hopke, Lara Gundel, John Ondov, and Petros Koutrakis. Mr. Robert Stevens, who is also a panel member, did not attend the meeting, but he submitted his comments in writing. Members of the speciation group, which consists of EPA staff and representatives from several states, also participated in this meeting. Below is a summary of the expert panel recommendations.

Overall, the panel was impressed with the progress made since the last review held in Seattle a year ago. Most of the panel and working group recommendations were considered and have been incorporated into the Guidance Document. The panel strongly believes that the goals, objectives, and monitoring strategy of the Speciation Network are sound and have been communicated to a great extent to the states and the scientific community. The revised Guidance Document will help to further inform the stakeholders about the different aspects of this program.

We feel that significant progress was made in many areas, including:

*Particle Measurements:* A list of particle measurement methods has already been developed and is included in the Guidance Document. This list is final and there is consensus about the particulate constituents to be measured.

*Sampling Frequency:* Increasing the sampling frequency from every sixth day to every third day will provide sufficient statistical power to detect trends, as discussed in the Guidance Document. Furthermore, increasing the sampling frequency to every day for several sites will make it possible to carry out longitudinal air pollution health effects studies. This new generation of observational investigations will allow the examination of associations between morbidity and mortality outcomes, and a large spectrum of fine particle components. The panel realizes that augmenting the sampling frequency will result in increasing the cost of the network and will be burdensome to the states; however, the panel strongly believes that collecting more samples per site will be crucial to the EPA's efforts to detect trends. Therefore, if needed, the number of sites could be less than 55 to reduce costs.

*Sampler Development:* EPA staff have been working very intensively over the last year to evaluate and improve several candidate sampling devices. To date, many design and operational problems have been solved and a comprehensive field intercomparison study has been completed. The findings of this study will enable EPA scientists to determine the accuracy and precision of these methods, as well as to recommend further improvements, if needed. Trends networks require data of great quality; thus, it is of paramount importance that the proposed sampling devices be tested fully prior to their implementation. In spite of all this progress, the panel believes that there remain a number of issues regarding the sampling strategy which should be addressed by the EPA, as discussed below.

*Laboratory Contracts:* The EPA is in the process of selecting several laboratories to support the

states in the preparation of the sampling media and the chemical analysis of the samples. Also, a couple of EPA laboratories which will participate in the quality assurance activities have been identified.

As discussed above, tremendous progress has been made since the inception of the speciation program. The panel recognizes that the development and implementation of a such a large network is very challenging and will require a great deal of effort in the future. A large number of issues have been successfully addressed; however, these efforts primarily have preoccupied the EPA staff, so there was little time to focus on implementation of the network, quality assurance, and data analysis. Considering the limited number of EPA staff available to support the speciation network, the panel feels that the focus should be different for each of the first four years:

*First Year, Network Design and Objectives:* During the first year, the EPA staff focused its efforts on the design of the speciation network. Last year at the Seattle meeting, the expert panel had the opportunity to review the objectives of the network and the list of measurement parameters.

*Second Year, Sampler Intercomparison Field Studies:* Since the Seattle meeting, a series of field studies have been conducted to evaluate the performance of the candidate sampling devices. In addition, the EPA staff has initiated the process of contracting the laboratories designated to perform the sampler preparation and chemical analysis.

*Third Year, Intercomparison Completion and Implementation of the First Ten Sites:* The focus should be on the completion of the sampler tests, completion of the sampling and analysis protocols, and start-up of the first ten sampling sites. An effort should be made to develop an implementation plan for the speciation network and to set up a managerial structure. It is important to present a structured plan outlining the responsibilities and duties of the participating groups.

*Fourth Year, Development of State Expertise in Particulate Data Interpretation:* State scientists have a tremendous experience in particle sampling and to, some extent, in chemical analysis methods; however, the state scientists have little experience in analyzing particulate data. Therefore, before the end of the fourth year, a plan should be presented to provide training to state scientists in source apportionment methodologies and their interpretation.

## **GUIDANCE DOCUMENT**

The revised draft Speciation Network Guidance Document represents a significant improvement over the previous versions and has incorporated many of the suggestions of the various advisory groups who have commented upon the earlier versions. In general, the panel was very pleased with the progress made since last year. Overall, the network goals and objectives, as well as the network design, were well presented. Moreover, the discussion on the sampling and analysis methods, quality assurance, and data analysis were very comprehensive. The panel members had a number of minor comments on the document, which have been submitted directly to the EPA staff.

The panel recommends that the Guidance Document remain a living document to be updated periodically. For instance, the document can be used to: (i) discuss changes in the sampling and analysis technologies; (ii) provide reports on the laboratory and field audits; (iii) discuss changes in the list of species to be measured; (iv) inform about the selection and initiation of the sites; (v) present summary results from the different sites; (vi) present lists of publications relevant to the network; etc.

Instead of continuously revising the document, it may be preferable to establish successive editions of the document (e.g., edition 1, 2, 3 . . .). This will make it possible to maintain a record of the evolution of the network, and thereby enable us to understand why, how, and when the different changes were made.

In order to sustain the production of the different editions in a cost-effective way, the panel offers the following suggestion: reduce the volume of the document to approximately fifty pages and use web link sites to provide the support information for the document. For example, the discussion on sampling methodology could be reduced from twenty pages to five if, at the end of this chapter, a link site was provided describing in detail the different methods. The link site-appended documents should be updated to reflect any changes which occur. If substantial revisions are necessary, then it would be desirable to have new editions for the appendices as well. Another example is the data analysis section. Here it is possible to present publications or data summaries by the link sites.

Furthermore, the order of the chapters should be changed. For example, the network design should be placed after the introduction, or be incorporated into the introductory section. The data analysis section should be placed after the sampling and data processing chapters. After reducing the text, the authors should ensure that there are no redundancies. Also, a couple of important components are missing, such as the overall managerial structure of the network and the implementation strategy of the network. These two important issues are addressed in the following section.

## **IMPLEMENTATION**

The panel recognizes the challenge of sustaining the focus and the quality of the network as it evolves. Therefore, the panel feels that the continuous involvement of the EPA and the working group will be imperative for the success of this large program. It was not clear, either from the presentations of the EPA staff or from the Guidance Document, what management team will be in charge of this network. To date, this program has been conceived and launched because of the creativity and commitment of several EPA staff members; yet, the panel feels that this is insufficient to fully develop and operate the speciation network. The panel proposes that a steering committee be formed as soon as possible. This committee should include scientists from OAQPS, ORD, and the states. As the speciation program makes a transition from the development stage to the implementation stage, the committee will be crucial in the effort to oversee and promote the network. The panel has been informed that an EPA Group on Standard Air Monitoring exists. Perhaps the speciation network committee, which will be accountable for the implementation of the speciation network, could report to this group.

It will be necessary for a number of scientists with well-defined responsibilities to be assigned permanently to the speciation network. The panel is concerned that if new EPA projects appear on the horizon, which frequently occurs, the staff currently involved with the speciation network may be reassigned to them. This would be detrimental to the network's continuity and success.

As mentioned above, implementation issues should be addressed during the third year of the program. Therefore, the next edition of the Guidance Document should include a section that will provide a formal structure and an organizational chart of the program. This section should address who is responsible for the day-to-day operations and who will monitor the overall success of the program. It also should address who will carry out the validation of the field data, how the data sets will flow from one group to another, and who will be responsible for their overall management.

## **EVOLUTION OF ANALYTICAL METHODS**

Fortunately, over the last few decades we have experienced substantial decreases of particle concentrations. It is likely that concentrations of particulate constituents will continue to decrease. An exception is nitrate concentrations which may increase due to the anticipated sulfur dioxide emission reductions. Ion chromatography, which is the preferred analytical technique for sulfate, nitrate, and ammonium, is sensitive enough and therefore will continue to be adequate even if concentrations of ionic species decrease by a factor of 10 to 20 times. This may not be the case for elements and carbon. Although XRF analysis is sensitive enough for crustal elements, it is not sensitive enough for trace elements. ICP/MS is a promising analytical technique that is more sensitive than XRF; however, it needs further validation. In addition, its performance on crustal elements is not as good as the XRF. Therefore, if concentrations continue to decrease we may have a serious problem. Similarly, for the carbon analysis of quartz filters, speciation samplers collecting at flow rates less than 16.7LPM may have sensitivity problems for a large number of sites.

Indeed, there are important analytical issues that need to be addressed by the EPA and the panel during the next year after the validation of the sampling techniques is completed. If changes in the chemical analysis scheme are to take place, then it will be necessary to establish rules to decide if and when change is necessary. For instance: When is it necessary to replace an analytical method? What happens to the data obtained from the previous methods? Do they become obsolete or can they be corrected? In an initial response to these questions, the panel suggested that changes be made only if they will help to meet the primary objectives of the network. For example, ICP/MS is more sensitive than XRF for heavy toxic metals, which is very important for health effects studies; however, if it is not suitable for crustal elements (future studies should examine this further), it cannot be used for the speciation network. This is because mass closure, which is one of the primary objectives of the network, requires the accurate determination of Si, Al, and other crustal elements.

In general the speciation network is more challenging than other trend networks because it comprises a large number of analytes. As a result, a great deal of effort will be necessary to balance network continuity and new technology. By developing guidelines based on which decisions can be made, it will be possible to overcome the large number of problems that will arise.

## SAMPLING

The panel suggests that the selection of the sampling devices for the speciation network should be based on performance criteria. The panel agrees, therefore, that more than one sampler type could be adopted for the trends network. If the precision and accuracy of the recommended speciation samplers are less than 10%, then different methods could be used for trends sites; however, the panel recommends that once a sampler is selected for a given trend site, it should be used permanently at that site, in order to detect yearly trends on the order of 1-3%. If a decision is subsequently made to replace the sampler or one or more of its components, the difference between the previous and the improved method must be documented. To do this, it will be necessary to collocate the two sampling techniques (or versions) for at least one year at that site to document their difference. This process will make it possible to incorporate the data from the two methods into the same trends data set.

Considering the current state of knowledge and technology, the panel anticipates that the sampling strategy of the speciation network will change, as discussed later in this report. Although being flexible and adaptive is one of the philosophies of the network, improving and modifying the sampling and analysis techniques in a trends network can be a difficult task. The panel has given some serious consideration to this issue. Although we provide some suggestions in this report, we plan to address this issue in a more comprehensive manner in a future report, after the results from the sampler intercomparison study and the proposed laboratory tests become available.

The decision to use performance criteria for the speciation network was based on the following reasons:

- Having the flexibility to employ more than one sampling technique in the speciation network will encourage researchers and manufacturers to continue the development of continuous and integrated technologies. The development of continuous measurement techniques for sulfate, nitrate, carbon, and other species will be critical in reducing both labor and analysis costs. These new continuous samplers could be used to replace one or more channels of the speciation samplers. For instance, if an accurate carbon monitor for both organic and elemental carbon becomes available, the quartz filters and the associated sampler components can be eliminated. Thus, as new technologies will emerge, it is conceivable that speciation platforms will consist of both integrated and continuous sampling techniques.
- The panel believes that the candidate samplers present more or less similar features and that, with some additional minor improvements, most of them will be suitable for the speciation network. This will provide the states an opportunity to select the samplers of their choice, which will in turn enhance competition and help decrease the cost for sampling devices.
- A large investment already has been made in the IMPROVE network. It is anticipated that data sets from previous and future measurements of this network will be used by

the speciation network. For this reason, some of the states had suggested that the IMPROVE sampler also be used for the speciation network. This is a sound proposal which has its obvious merits and still remains a possibility. By allowing the use of more than one sampling device, the states will have the option to use the IMPROVE sampler, with which they already are familiar.

One of the drawbacks of selecting more than one sampler for the speciation network is that it will be necessary to develop and implement separate field and sampler handling protocols for each method. Although this will not have an impact on the states, it definitely will be an extra burden to the laboratories and the QA/QC staff.

Below we present a series of performance criteria that can be used by the EPA for both the trends and SIP assistance sites. Since the speciation network is not a compliance one, we suggest the use of the term “recommended sampler” instead of “equivalent sampler.” The process for sampler endorsement from the EPA should be less complicated than for equivalency. If the performance criteria, which are specified below, are met by a sampling device, that sampler should automatically be designated as recommended. Continuous monitors, which measure one or more species, also can be recommended methods if they meet the performance criteria for the species they measure.

To date, the panel believes that the candidate samplers are not fully tested; however, the panel realizes that there is an urgency to start the implementation of the speciation network. Therefore, the panel proposes that two sets of performance criteria be applied to candidate samplers:

The first set of performance criteria should focus on the ability of the sampling devices to collect fine particle mass, sulfate, and elements. These evaluations will be based on a series of field studies which already have been conducted, and laboratory tests which can be completed before the end of summer 1999. The panel believes that collecting fine particles for elemental analysis should be easier than collecting ions and carbon.

The second set of performance criteria focuses on the ability of the sampling devices to collect carbonaceous aerosols and nitrate. For these evaluations it will be necessary to conduct a number of laboratory and field studies which will evaluate the performance of the nitric acid and organic carbon denuders. While the criteria for the nitric acid denuder are well understood and are presented below, this is not the case for the organic carbon denuder. As discussed below, there are still many unresolved technological and conceptual issues regarding the use of organic carbon denuders. For this reason, the proposed criteria could be modified as our scientific understanding evolves.

Therefore, as we review the results of future tests, these criteria may change and the samplers may have to be modified, for example, to include a carbon denuder. The manufacturers of sampling devices should be informed about the potential changes so that their current designs allow for future changes.

### *Elements/Mass:*

The channel for the elemental analysis is the simplest because it does not require the use of a denuder, since most of the elements are not volatile; however, the Teflon filter of this channel should collect the same fine mass as the FRM. The same requirement applies for all three channels (elements, ions, and carbon). As recommended by the first panel report last year, the size cut-off characteristics of the different inlets of the speciation samplers should be similar to those of the FRM. Therefore, it is important that the manufacturers of the different speciation samplers provide results from laboratory tests that report the collection efficiency and losses as a function of the particle size for each of the speciation channels of the sampler. Some of the inlets that have been used by the speciation samplers may already have been tested; however, considering the complexity of some of the samplers (e.g., too many lines, split flows which may not be isokinetic, etc.), the panel believes that the system performance needs to be tested for particle cut-off characteristics and losses.

### *Performance Criteria for Elements/Mass:*

The performance criteria for these laboratory tests are:

- First:* The inlet cut-point and separation profile for the candidate method must be comparable to the WINS inlet. A number of laboratory and field tests should be conducted to demonstrate that the fine particle mass samples collected by the speciation monitor and the FRM are in good agreement. The following two criteria must be met for the candidate method to be acceptable: 1) based on linear regression, the  $R^2$  value must be  $\geq 0.9$  and; 2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be  $1.0 \pm 0.1$ . At least twenty 24-hour duration samples should be used for the regression analysis.
- Second:* The particle size cut-off should be  $2.5 \pm 0.5 \mu\text{m}$ ; the sharpness of the collection efficiency curve should be at least as good as the FRM; particle losses should be less than 10% for particle sizes between 0.1 and 2.5 microns. These tests should be done for the entire channel and not just for the particle selective inlet (impactor or cyclone). If channels are not identical, each channel should be tested separately.
- Third:* If cyclones or impactors are used for the collection of multiple samples, the capacity of these particle separators should be tested. Although there are many ways to determine the capacity of these samplers, we propose the following test. Use a nebulizer to aerosolize and aqueous suspension of polydisperse glass beads (these commercially available particles have a nominal size range of 3-10  $\mu\text{m}$ , but the number distribution of smaller sizes is adequate for these tests, with density about 2.5g/cc). The generated particles should be diluted in a clean air stream of 20-30% RH. Measure the particle size distribution and number upstream and downstream the channel as a function of time. Particle concentrations should be



three to four hundred times higher than the ambient ones, so that experiments can be completed in a day. By examining the sampler particle size cut-off as a function of time, it is possible to estimate the particle capacity. When the sampler size cut-off gradually starts to increase, this is an indication of particle bounce. This point will correspond to a certain total amount of particle mass removed by the cyclone or impactor. To be conservative the capacity of the sampler can be designated as half of this mass value. The use of glass particles at low RHs make this experiment a realistic simulation of the real atmosphere. A different approach is to measure the sampler particle cut-off characteristics every two months in order to determine capacity. According to Dr. Cahill, former Principal Investigator of IMPROVE, the capacity of cyclones has been tested and determined to be adequate for a year of sampling, but these data were never published.

*Fourth:* Although it is not required, it is desirable that the sampler collect particles at a face velocity and flow similar to that of the FRM-PM<sub>2.5</sub>.

#### *Sulfate Sampling:*

Sulfate is one of the most robust particle species because it remains stable during and after sampling. For this reason, no sampling problems are anticipated.

#### *Performance Criteria for Sulfates:*

A number of laboratory and field tests should be conducted to demonstrate that the sulfate collected by the candidate speciation monitor and the FRM are in good agreement. For sulfate the following two criteria must be met for the candidate method to be acceptable: (1) based on linear regression, the R<sup>2</sup> value must be  $\geq 0.95$ ; and (2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be  $1.00 \pm 0.05$ . At least twenty 24-hour duration samples should be used for the regression analysis.

#### *Nitrate Sampling:*

In contrast to sulfate, nitrate sampling is quite challenging. Although nitrate concentrations currently are high only in the Western U.S., it is anticipated that in the future they will increase substantially in the Northeastern U.S., due the projected sulfur dioxide emission reductions. Accurate measurements of nitrate require the removal of gas phase nitric acid prior to particle collection. They also require the collection of nitrate on a filter medium, such as a nylon filter or sodium carbonate coated filter, which bind nitric acid molecules produced during the volatilization of the collected particulate ammonium nitrate. Removal of the gaseous nitric acid can be achieved by diffusion denuders coated with alkaline substances (e.g., sodium carbonate) or (unanodized) aluminum inlets. Previous methods which have used Teflon or glass fiber filters are negatively biased due to the ammonium nitrate loss during and after sampling. The equilibrium between particle ammonium

nitrate, gaseous ammonia, and nitric acid can be perturbed by changes in relative humidity and temperature. Loss of ammonium nitrate also can be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media. Nitrate, as well as other semi-volatile compounds, can be lost after sampling during shipping and storage. To date, there is no agreement among the different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling methods. Therefore, the nitrate sampler should include a nitric acid denuder and a nylon filter. If the speciation sampler relies upon metallic denuders that will be used for long periods of time (e.g., more than a couple of weeks, as with the IMPROVE network), the capacity of these denuders should be determined through laboratory and field studies.

#### *Performance Criteria for the Nitric Acid Denuder:*

The collection efficiency of the nitric acid denuder can be tested easily in the laboratory. Nitric acid permeation tubes are commercially available and can be used to expose the test denuders. Also, it is possible to nebulize solutions of nitric acid (Koutrakis, et al., 1998). This method presents several advantages, such as: (i) generation of a high dynamic range of nitric acid concentrations; (ii) easy control of concentration levels; and (iii) production of a relatively constant output and low cost. Since the collection performance of a nitric acid denuder is superior at high RHs, it is suggested that laboratory experiments be conducted at low RHs, 20-30%. Because the concentration of gas phase nitrate is usually higher than that of particulate nitrate, it is necessary for the denuder to have a collection efficiency higher than 99%. [The collection efficiency is equal to  $1 - C_{out}/C_{in}$ , where  $C_{out}$  and  $C_{in}$  are the nitric acid concentrations at the exit and entrance of the denuder.] Even a penetration of 1% of nitric acid can affect the nitrate measurement. For example, if we assume a nitric acid concentration of 25ppb, 1% will correspond to  $0.65 \mu\text{g}/\text{m}^3$  of nitrate. Considering that nitrate concentrations are typically in the range of a few  $\mu\text{g}/\text{m}^3$ , the collection of a small fraction of gas phase nitric acid on the nylon filter may result in significant overestimation of the particulate nitrate concentrations.

The denuder capacity is defined as the amount of nitric acid collected on the denuder before its collection efficiency starts to decrease. A conservative calculation of the nitric acid denuder must be done for the following two reasons: first, the denuder capacity is not always the same and depends upon the history of the denuder; and, second, nitric acid denuders may collect other acidic gases, such as sulfur dioxide, nitrous acid, and low molecular weight organic acids (e.g., formic and acetic acid). For this reason, the experimentally determined capacity should be divided at least by a factor of five. Assuming a nitric acid concentration of 25ppb and a use of 2,880 hours (24 hrs x 120 days/per one year), the capacity of the nitric acid should be 72 ppm/hr. Using a safety factor of 5, the capacity should be 360 ppm·hr. For a flow of 16.7 LPM, this corresponds to a collection of approximately 915 mg of nitric acid per year. Assuming that the only about 10% of the denuder coating material can be used before the collection efficiency deteriorates significantly, one would expect that about 15 grams (equivalent of sodium carbonate) of the coating substance will be necessary to coat the denuder.

There are two types of denuders: (a) the first type includes the denuders that have a relatively low capacity, such as sodium carbonate coated denuders, and therefore can only be used for a few days; and (b) the other denuders, such as (unanodized) aluminum denuders and magnesium oxide coated denuders, can have much higher capacity, and thus can be used for periods of up to a year. The high capacity denuders are more desirable, since they do not require frequent cleaning and coating; however, they must be fully validated prior to their implementation into the network. Laboratory tests can be conducted to examine the efficiency and capacity of the denuders. For low capacity denuders, laboratory tests are easy to perform. For nitric acid, the best way is to use a continuous chemiluminescent  $\text{NO}_x$  instrument to measure the nitric acid concentration upstream and downstream of the denuder. For these low capacity denuders (which have over 99% collection efficiency in the 200ppb nitric acid range) using upstream concentrations of about 200ppb nitric acid, the capacity of the annular denuder could be determined in a few hours. For high capacity denuders, longer exposure periods (several days or longer) and higher concentrations levels will be necessary; however, any denuder will maintain its given collection efficiency only for upstream concentrations below some upper limit. For concentrations above this value, the efficiency will decrease with increasing concentration, regardless of exposure duration, because the coating cannot stabilize the collected gas rapidly enough. Before testing the high capacity denuders, this upper limit must be determined (it is likely to be on the order of a few ppm). If we assume that the highest upstream nitric acid concentration that can be used is 2 ppm, then for the 360 ppm/hr estimated above (for use for 120 sampling days in a year), it would take 180 hr before the collection efficiency of the high capacity denuder would start to decrease. In general, the candidate denuder should not be used for field sampling until it has been characterized adequately using such laboratory tests. If complete laboratory testing validation is not feasible, then validation can be accomplished in conjunction with field tests. These tests need to be conducted at a site with relatively high nitric acid concentrations. One simple method would be to have simultaneous sampling with twelve denuders. Every month (up to a year) one of the denuders should be returned to the laboratory for testing, using the same technique (i.e., 200ppb nitric acid) as is used for low capacity denuders, measuring with the continuous monitor upstream and downstream of the denuder. If, after a certain number of months, the denuder efficiency drops significantly, this result determines the useful lifetime of the denuder (with a safety factor of at least 2 months).

*Reference Method for Nitrate Measurement:*

The reference method for nitrate measurement should include a WINS sampler, a sodium carbonate/glycerol-coated glass denuder, and a filter pack containing a sodium carbonate coated glass fiber filter or a nylon filter. The Teflon/Nylon or Teflon/sodium carbonate configuration is not appropriate because a large fraction of nitrate (20-40%) can be lost on the screen that separates the first and the second filter. Therefore, the use of a denuder with a single alkaline filter is an adequate reference method.

### *Performance Criteria for the Nitrate Measurement:*

For nitrate, the following two criteria must be met for the candidate method to be acceptable: (1) based on linear regression, the  $R^2$  value must be  $\geq 0.9$ ; and (2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be  $1.0 \pm 0.1$ . At least 24-hour duration samples should be used for the regression analysis.

### *Ammonium Sampling:*

Ammonium sulfate salts are very stable, so ammonium losses from these salts during sample collection and storage are negligible; however, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage. The extent of dissociation of ammonium nitrate depends on many parameters, including temperature, relative humidity, and face velocity for the collecting filter. Thus, one would expect that current sampling techniques underestimate ammonium concentrations due to the volatilization of ammonium nitrate. Fine particle mass typically contains many acidic compounds. Consequently, a fraction of volatilized ammonium (in the form of ammonia) can be retained on the Teflon filter by reacting with the acid compounds. Therefore, it is reasonable to assume that ammonium loss is less than the nitrate loss.

Preliminary results suggest that placing an alkaline filter (nylon or sodium carbonate coated filter) directly below the Teflon filter, without using a separation screen, enhances the volatilization of ammonium nitrate from the Teflon filter (preliminary results from the Bakersfield CARB intercomparison study). Under these conditions, the majority of ammonium nitrate leaves the Teflon filter, and only a small fraction of ambient ammonium is measured. Even though volatilization losses are less with the use of a separation screen, the losses are still very significant.

### *Reference Method for Ammonium Measurement:*

The reference method for ammonium measurement should include a WINS sampler, a citric acid/glycerol-coated denuder, and a filter pack containing a single citric acid/glycerol-coated glass fiber filter.

### *Performance Criteria for the Ammonium Measurement:*

The candidate speciation samplers do not measure ammonium directly. Rather, the ammonium will be estimated; however, if future techniques make it possible to measure ammonium directly, the performance criteria are as follows: A number of laboratory and field tests should be conducted to demonstrate that the ammonium collected by the speciation monitor and the ammonium reference method (described above) are in good agreement. For ammonium, the following two criteria must be met for the candidate method to be acceptable: (1) based on linear regression, the  $R^2$  value must be  $\geq 0.9$ ; and (2) the ratio of the mean concentration for the candidate method to the mean for the reference method must be  $1.0 \pm 0.1$ . At least 24-hour duration samples should be used for the regression analysis.

### *Carbon Sampling:*

Accurate mass balance and quality assurance require determination of particulate (total) carbon,  $C_t$ , because of its abundance. Differentiation of organic,  $C_o$ , elemental,  $C_e$ , and carbonate carbon,  $C_c$ , provides more useful characterization for trends analysis and source apportionment. Semi-volatile species ( $C_{sv}$ ) compose a fraction of the organic carbon which exists in the atmosphere with a partition between particle and gas phases. This partition is extremely complex, and depends on temperature, vapor pressures of individual species, the absolute and relative concentrations of all of the different species, and the amounts and types of adsorbing particle surfaces. The amount of the particulate phase of these species collected on the (first) filter depends on sampling conditions (e.g., filter face velocity).  $C_{sv}$  is defined as the carbon that is collected on sorbent traps downstream of the filters on conventional samplers.

Carbonaceous particles are commonly collected on a series of two quartz filters. Presumably, the first collects all of the particle phase carbon (elemental and organic) and a very small fraction of gas phase organic carbon. Likewise, the second quartz filter is supposed to collect only the same small fraction of gas phase organic carbon as collected by the first filter. Therefore, the concentration or particle phase organic carbon is calculated by subtracting the amount of organic carbon on the second from that of the first stage; however, this assumption does not take into account particle phase organic carbon that can volatilize from the first filter and gets collected by the second quartz filter. To the extent that this volatilization occurs, it results in underestimation of particle phase organic carbon.

The use of two quartz filters for organic carbon measurements is questionable. Eatough, et al. (1989) and Tang, et al. (1994) concluded that desorption of organic gases from particles on the first quartz filter was the dominant sampling artifact (negative artifact), while Turpin, et al. (1994) suggested that organic gases can be collected by the quartz filter (positive artifact). Turpin, et al. found that adsorbed organic gases represent up to 50% of the organic carbon measured on quartz filters in southern California. This study suggested that: (1) organic gas absorption (positive bias) was much larger than organic particle volatilization (negative bias); (2) as sample durations increase, the fraction of the adsorption bias decreases because the filter becomes saturated; and (3) the magnitude of the bias depends on the composition of the organic gases and particles present in the air sample. We currently do not know to what extent the use of the second quartz filter improves the accuracy of the organic carbon measurements. For this reason, the expert panel last year recommended to analyze only one of the first quartz filters in order to reduce analytical costs.

The diffusion denuder approach may be a sound approach to overcome the problems mentioned above. According to this sampling technique, gaseous organic compounds are removed using an activated carbon or XAD coated diffusion denuder. Subsequently, the particle-phase organic carbon can be collected downstream of the denuder using a series of two quartz filters. The first filter collects particle phase organic carbon, while the second collects the organic carbon volatilized from the first quartz filter. The total particle carbon concentration is determined by adding the concentrations of the first and second filter, respectively.

During the meeting Dr. Charles Lewis, of the EPA, presented some very interesting comparisons between the different candidate carbon samplers and a sampler which was equipped with an XAD-coated organic carbon denuder. Although these results were preliminary, it was clear that organic carbon concentrations obtained from the denuder/sampler were lower, on the order of 30-50%, than those from the candidate samplers. Organic carbon concentrations obtained from the candidate samplers were not in a very good agreement, with differences of more than 20-30%. It is possible that these discrepancies could have resulted from use of different face velocities across the sample filter(s). In last year's report, the panel had underlined the need for the samplers to employ filter face velocities similar to the FRM. In contrast to organic carbon measurements, elemental carbon concentrations obtained from the denuder/sampler and the candidate samplers were in a good agreement. It is worth mentioning that the collection efficiency and capacity of the XAD-coated organic carbon denuder is not yet well-characterized. Also, it is not known whether removing gas phase organics prior to particle collection enhances the volatilization of organic carbon from the quartz filter. Such an effect also would have resulted in lower organic carbon concentrations.

While these conclusions are drawn from the presentation of preliminary results, there is good indication that further development is required to have an adequately characterized, accurate sampler for carbonaceous aerosols; however, even such a technology were available, it is not certain that it would be appropriate. This is because it is not known whether the same amount of organic carbon is lost from the Teflon filter used as the collection medium for the FRM. Until we have a better understanding of organic carbon artifacts for the FRM and the speciation sampler (one quartz filter with no denuder) it will be unwise to recommend the use of the denuder for the speciation sampler. If negligible amounts of organic carbon are lost from the Teflon filter, then it will be desirable to use an accurate speciation sampler. This will make it possible to achieve a better mass closure (the sum of particle constituents collected by the speciation sampler should be equal to the mass measured by the FRM); however, if substantial amounts of organic carbon are lost from the Teflon filter of the FRM, then it will be very difficult to achieve closure. Indeed, the majority of the data that exist suggests that it is difficult to achieve closure and that the discrepancies can go both ways (Andrews, et al., in press). This suggests that artifacts for the Teflon and quartz filters are not the same. This can be a problem for the speciation sampler because the FRM is by definition the "gold standard." For example, let us assume that a state finds out that organic carbon constitutes a large fraction of the fine mass. If the speciation sampler is accurate but a large fraction of the organic carbon is lost from the Teflon filter, then a sound source reduction strategy may not be successful in terms of enabling that state to comply with the standard. The same result will occur if the speciation sampler overestimates organic carbon but the FRM is accurate. These two extreme situations illustrate the complexity of the problem. One can imagine that the situation would be even more complicated if each method has a different bias. In such a case we would be faced with both scientific and legal problems.

The intent of this discussion is not to challenge the validity of the FRM. The gravimetric method was rightfully selected because the results of the epidemiological studies on which the standard was based used mass measurements obtained from gravimetric analysis. Our intent is to stress the need for developing accurate organic carbon sampling methods and to anticipate some of the challenges we will face as we proceed with the implementation of the speciation network.

*Performance Criteria for the Organic Carbon Sampler (Including Organic Carbon Denuder):*

Field and laboratory studies currently are being conducted in Seattle, WA, to evaluate novel sampling and analysis techniques for organic carbon. A number of speciation and research samplers have been selected for these tests. These investigations will test the capacity and efficiency of XAD and carbon-impregnated filter denuders. These studies are also designed to determine the contribution of semi-volatile organic carbon to the total organic carbon concentrations and its partition coefficient between the gaseous and particulate phases. The results of these studies should make it possible to develop performance criteria for organic carbon samplers, including criteria for evaluating the capacity and efficiency of the organic carbon denuders. Developing performance criteria for denuder performance evaluation is a challenging task for the following reasons: first, the denuder must perform for a large number of organic compounds (currently we have limited knowledge about the identity and concentrations of these compounds); second, the collected compounds on the denuder surface may be de-adsorbed (the rate of de-adsorption depends on organic compound, denuder capacity, total gas phase organic concentration, temperature, and relative humidity).

Furthermore, the question of volatilization of organics from the Teflon filter in the FRM is one that should be explicitly addressed in upcoming field studies. The question of organic carbon loss can be answered by collecting carbon on a sorbent downstream the Teflon filter. Such tests are currently conducted in Seattle; however, similar tests should be conducted in other U.S. environments. The results of these tests will be crucial to our ability to develop performance criteria of organic carbon sampling.

*Sampling Strategy:*

Recognizing that sampling must be initiated in the near future, the panel supports the use of the current state-of-the-art technology. Although it is necessary to start out using this current methodology, the speciation network should be open to new, validated, more accurate technologies as they become available. In contrast to compliance networks, the speciation network is not bound to use Federal Reference Methods which cannot easily be changed. The speciation network needs to have the flexibility to be updated as the technology and our understanding evolve. To carry this out we must first develop a set of performance criteria to evaluate current and future sampling technologies and second, we have to enhance our understanding of the biases of the different methods. This will make it possible to upgrade the network, when appropriate, without affecting the consistency of data.

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